

**This Page Is Inserted by IFW Operations  
and is not a part of the Official Record**

## **BEST AVAILABLE IMAGES**

**Defective images within this document are accurate representations of the original documents submitted by the applicant.**

**Defects in the images may include (but are not limited to):**

- **BLACK BORDERS**
- **TEXT CUT OFF AT TOP, BOTTOM OR SIDES**
- **FADED TEXT**
- **ILLEGIBLE TEXT**
- **SKEWED/SLANTED IMAGES**
- **COLORED PHOTOS**
- **BLACK OR VERY BLACK AND WHITE DARK PHOTOS**
- **GRAY SCALE DOCUMENTS**

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

**THIS PAGE BLANK (USPTO)**

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

**EP 0 926 107 A2**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
30.06.1999 Bulletin 1999/26

(51) Int Cl.<sup>6</sup>: **C04B 35/46**, C03C 3/089,  
H01G 4/12

(21) Application number: **98123587.2**

(22) Date of filing: **10.12.1998**

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE**  
Designated Extension States:  
**AL LT LV MK RO SI**

(30) Priority: **11.12.1997 JP 34149197**  
**04.11.1998 JP 31333998**

(71) Applicant: **Murata Manufacturing Co., Ltd.**  
**Nagaokakyo-shi Kyoto-fu 617-8555 (JP)**

(72) Inventors:  
• **Sugimoto, Yasutaka**  
**c/o Murata Manufacturing Co.Ltd**  
**Nagaokakyo-shi, Kyoto-fu 617-8555 (JP)**

• **Sunahara, Hirofumi**  
**c/o Murata Manufacturing Co.Ltd**  
**Nagaokakyo-shi, Kyoto-fu 617-8555 (JP)**  
• **Sugou, Kimihide**  
**c/o Murata Manufacturing Co.,Ltd.**  
**Nagaokakyo-shi, Kyoto-fu 617-8555 (JP)**  
• **Takagi, Hiroshi**  
**c/o Murata Manufacturing Co.,Ltd.**  
**Nagaokakyo-shi, Kyoto-fu 617-8555 (JP)**

(74) Representative: **Laufhütte, Dieter, Dr.-Ing. et al**  
**Lorenz-Seidler-Gossel**  
**Widenmayerstrasse 23**  
**80538 München (DE)**

(54) **Dielectric ceramic composition and ceramic electronic parts using the same**

(57) A dielectric ceramic composition is formed of a mixture including a BaO-TiO<sub>2</sub>-REO<sub>3/2</sub> ceramic composition, wherein RE represents a rare earth element, and a glass composition containing about 13-50 wt.% SiO<sub>2</sub>, about 3-30 wt.% B<sub>2</sub>O<sub>3</sub>, about 40-80 wt.% alkaline earth

metal oxide, and about 0.5-10 wt.% Li<sub>2</sub>O. The dielectric ceramic composition has a high dielectric constant and a high Q value, as well as excellent temperature stability, and is capable of being sintered at a relatively low temperature. The dielectric ceramic composition is advantageously used in ceramic electronic parts.

**EP 0 926 107 A2**

## Description

[0001] The present invention relates generally to a dielectric ceramic composition, which is a glass-ceramic composite material for low temperature firing, more particularly, to a dielectric composition for use in a microwave resonator, a LC filter, a laminated capacitor, and a multilayered circuit board or the like.

[0002] With miniaturizing of the electronic devices such as a microwave resonator and a microwave filter, efforts have been made to replace cavity resonators with ceramic dielectrics having a high relative dielectric constant. Resonators and the filters are miniaturized by use of an effect that a wavelength of electromagnetic waves in dielectrics is shortened to  $1/\epsilon^{1/2}$  times that in free space, wherein  $\epsilon$  represents the relative dielectric constant of dielectrics.

[0003] However, the dielectric material has not met a recent demand for further miniaturization since the relative dielectric constant  $\epsilon$  of a ceramic dielectric material having a temperature coefficient suitable for use as a dielectric resonator has so far been limited to 100 or less.

[0004] A method employing an LC resonator, which has conventionally been known in microwave circuits, is effective for meeting the demand under restriction of a relative dielectric constant  $\epsilon$  of a ceramic dielectric material. Thus, a further miniaturized electronic apparatus having high reliability may be produced by applying to fabrication of LC circuits a lamination method which is adapted in practice for a laminated capacitor and a multilayered board.

[0005] However, producing by way of a lamination method an LC resonator having a high Q value in a microwave region requires high electric conductivity of an internal electrode which is built into a laminated capacitor and a multilayered circuit board. A metal having high electric conductivity such as gold, silver, or copper must be used for an internal electrode which is fired simultaneously with a dielectric or a multilayered circuit board. For this reason, a dielectric material must be able to be sintered at low temperature simultaneously with internal electrodes formed of a metal material having a low melting point, and as well must have a high dielectric constant, a high Q value, and enhanced temperature stability. However, a dielectric material which meets all of these criteria has not yet been found.

[0006] An object of the present invention is to provide a dielectric ceramic composition which has a high relative dielectric constant, a high Q value, and temperature stability, and which is capable of being sintered at relatively low temperature.

[0007] Another object of the present invention is to provide ceramic electronic parts which have excellent high-frequency characteristics and are able to be miniaturized.

[0008] In one aspect of the present invention, there is provided a dielectric ceramic composition formed of a mixture comprising a first  $\text{BaO-TiO}_2\text{-REO}_{3/2}$  ceramic composition (RE represents a rare earth element) and a glass composition, wherein the glass composition comprises about 13-50 wt.%  $\text{SiO}_2$ , about 3-30 wt.%  $\text{B}_2\text{O}_3$ , about 40-80 wt.% alkaline earth metal oxide, and about 0.5-10 wt.%  $\text{Li}_2\text{O}$ . Examples of rare earth elements RE include Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, and these elements may be used singly or in combination as desired.

[0009] Preferably, the above-described dielectric ceramic composition contains CuO as a secondary component.  
[0010] The above-described first  $\text{BaO-TiO}_2\text{-REO}_{3/2}$  ceramic composition may be represented by  $x\text{BaO-yTiO}_2\text{-zREO}_{3/2}$ , wherein x, y, and z are based on mole% and satisfy the following relations:  $5 \leq x \leq 15$ ,  $52.5 \leq y \leq 70$ ,  $15 \leq z \leq 42.5$ ; and  $x + y + z = 100$ , and contains PbO in an amount of 20 parts by weight or less with respect to 100 parts by weight of the first ceramic composition.

[0011] The alkaline earth metal oxide contained in the above-described glass composition preferably comprises BaO and at least one species selected from the group consisting of SrO, CaO, and MgO, and the compositional proportions of SrO, CaO, MgO, and BaO fall within the ranges of about 35 wt.% or less, about 35 wt.% or less, about 20 wt.% or less, and about 40-95 wt.%, respectively.

[0012] The above-described dielectric ceramic composition is preferably such that the first ceramic composition accounts for about 80-95 wt.%, the glass composition accounts for about 5-20 wt.%, and CuO accounts for about 3 wt.% or less.

[0013] Preferably, the dielectric ceramic composition of the present invention further comprises at least one species of a ceramic compound selected from the group consisting of  $\text{TiO}_2$ ,  $\text{CaTiO}_3$ ,  $\text{SrTiO}_3$ , and  $\text{Nd}_2\text{Ti}_2\text{O}_7$ . As used herein, these ceramic compounds are referred to as "second ceramic compositions" for the sake of making contrast with the aforementioned first ceramic composition.

[0014] In this case, the first ceramic composition accounts for about 50-95 wt.%, the glass composition accounts for about 5-20 wt.%, CuO accounts for about 3 wt.% or less, and the second ceramic composition accounts for about 30 wt.% or less.

[0015] In another aspect of the present invention, there is provided a ceramic electronic part characterized by utilizing as a dielectric ceramic layer the dielectric ceramic compositions.

[0016] According to the present invention, since a dielectric ceramic composition is formed of a mixture comprising a first  $\text{BaO-TiO}_2\text{-REO}_{3/2}$  ceramic composition (RE represents a rare earth element) and an  $\text{SiO}_2\text{-B}_2\text{O}_3$ -alkaline earth metal oxide- $\text{Li}_2\text{O}$  glass composition, it can be sintered at a temperature lower than the melting point of an electric conductor containing, as a primary component, one of a low-specific-resistance metal selected from silver, gold, and

copper. Moreover, the present invention successfully provides a dielectric ceramic composition having a high relative dielectric constant within a high-frequency region, particularly within a microwave region and a millimeter wave region, as well as excellent temperature stability.

[0017] Addition of CuO, as a secondary component, to the mixture comprising a first ceramic composition and a glass composition further lowers sintering temperature of the resultant mixture and increases the Q value and the relative dielectric constant thereof.

[0018] Therefore, when used as a dielectric ceramic layer, such a dielectric ceramic composition can be fired simultaneously with a low-specific-resistance internal electrode made of gold, silver, copper, etc., to thereby yield ceramic electronic parts such as dielectrics and multilayer circuit boards containing such an internal electrode therein and having excellent high-frequency characteristics. Ceramic electronic parts such as LC resonators and LC filters having a high Q value can be further miniaturized by use of a lamination method and the dielectric ceramic composition as a dielectric ceramic layer.

[0019] In the present invention, the above-described dielectric ceramic composition encompasses a powder comprising a mixture of the first ceramic composition and the glass composition (optionally the second ceramic composition); a paste composition in which the powder composition is dispersed in a medium such as an organic vehicle; a ceramic green sheet obtained by forming the paste composition; and a ceramic composition obtained by firing the green sheet.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0020]

Fig. 1 is a ternary diagram of a BaO-TiO<sub>2</sub>-REO<sub>3/2</sub> ceramic composition;  
 Fig. 2 is a fragmentary perspective view of an LC filter employing the ceramic electronic parts of the present invention;  
 Fig. 3 is a schematic perspective view of the LC filter; and  
 Fig. 4 is a circuit diagram of the LC filter.

[0021] Fig. 1 shows a ternary diagram referring to the compositional ranges of a first BaO-TiO<sub>2</sub>-REO<sub>3/2</sub> ceramic composition which is a primary component of the first ceramic composition used in the dielectric ceramic composition according to the present invention. The compositional proportions of the BaO-TiO<sub>2</sub>-REO<sub>3/2</sub> ceramic composition, when represented by xBaO-yTiO<sub>2</sub>-zREO<sub>3/2</sub>, are such that x, y, and z fall within the ranges satisfying  $5 \leq x \leq 15$ ,  $52.5 \leq y \leq 70$ ,  $15 \leq z \leq 42.5$ ; and  $x + y + z = 100$  on a mole % basis, and the composition preferably falls within the domain indicated by oblique lines in Fig. 1.

[0022] In contrast, a composition falling within the domain A is difficult to sinter and in some cases does not provide a porous ceramic even at 1400°C, which is the conventional sintering temperature. When a composition falls within the domain B, a temperature-dependent characteristic, i.e., a temperature coefficient of dielectric constant of a capacitor formed inside a multilayered circuit board, tends to decrease drastically onto the negative side. When a composition falls within the domain C, the relative dielectric constant is extremely small and in some cases the sintered property is not good. Furthermore, when a composition falls within the domain D, the temperature coefficient of dielectric constant increases drastically onto the positive side and the relative dielectric constant tends to decrease.

[0023] The first ceramic composition used in the dielectric ceramic composition according to the present invention preferably contains about 20 parts by weight or less of PbO in addition to a BaO-TiO<sub>2</sub>-NdO<sub>3/2</sub> ceramic composition which falls within the compositional domain indicated by oblique lines in Fig. 1. In practice, addition of PbO provides a dielectric ceramic composition having more stabilized characteristics; however, addition of PbO in excess of 20 parts by weight makes the temperature coefficient of change in dielectric constant negative and high, and the Q value decreases.

[0024] The glass composition will next be described. The glass composition comprises about 13-50 wt.% SiO<sub>2</sub>, about 3-30 wt.% B<sub>2</sub>O<sub>3</sub>, about 40-80 wt.% alkaline earth metal oxide (BaO, SrO, CaO, MgO), and about 0.5-10 wt.% Li<sub>2</sub>O.

[0025] B<sub>2</sub>O<sub>3</sub> contained in the glass composition lowers the glass viscosity and accelerates sintering of a dielectric ceramic composition. However, when the content of B<sub>2</sub>O<sub>3</sub> is in excess of about 30 wt.%, moisture resistance is adversely affected; whereas when it is less than about 3 wt.%, the composition is not sintered at about 1000°C or less.

[0026] When the content of SiO<sub>2</sub> is in excess of about 50 wt.%, the glass softening temperature increases drastically and ceramic compositions containing SiO<sub>2</sub> in such a high amount cannot be sintered; whereas when it is less than about 13 wt.%, moisture resistance is adversely affected.

[0027] The alkaline earth metal oxide promotes reaction between the ceramic composition and the glass composition and lowers the softening point of the glass composition. When the content of the alkaline earth metal oxide is less than about 40 wt.%, the sintered property decreases to induce difficulty in sintering at about 1000°C or less; whereas when

it is in excess of about 80 wt.%, moisture resistance is adversely affected.

[0028] When the content of BaO in the alkaline earth metal oxide is in excess of about 95 wt.%, moisture resistance is adversely affected; whereas when it is less than about 40 wt.%, the sinterability might decrease. In view of moisture resistance, the composition preferably contains at least one species among SrO, CaO, and MgO in an amount of about 5 wt.% or more.

[0029]  $\text{Li}_2\text{O}$  lowers the glass softening point. However, when the  $\text{Li}_2\text{O}$  content is in excess of about 10 wt.%, moisture resistance is unsatisfactory; whereas when it is less than about 0.5 wt.%, the softening point increases drastically to prevent sintering.

[0030] When the amount of the glass composition contained in the dielectric ceramic composition is less than about 5 wt.%, sintering might be difficult; whereas when it is in excess of about 20 wt.%, moisture resistance might deteriorate to lower the relative dielectric constant.

[0031] CuO also functions as a sintering aid. When the content is in excess of about 3 wt.%, the Q value tends to decrease to shift the temperature coefficient of dielectric constant to a high positive value.

[0032] Each of  $\text{TiO}_2$ ,  $\text{CaTiO}_3$ , and  $\text{SrTiO}_3$  which serve as the second ceramic composition has a negative temperature coefficient of dielectric constant, whereas  $\text{Nd}_2\text{Ti}_2\text{O}_7$  is a composition having a positive temperature coefficient of dielectric constant. Briefly, in the present invention, there is incorporated, as an additive for modifying temperature characteristic, at least one species of a second ceramic composition selected from the group consisting of  $\text{TiO}_2$ ,  $\text{CaTiO}_3$ ,  $\text{SrTiO}_3$ , and  $\text{Nd}_2\text{Ti}_2\text{O}_7$ , in an appropriate amount into a mixture comprising the first ceramic composition and the glass composition, to thereby preset the temperature characteristic of the dielectric ceramic composition of the present invention to a desired value.

[0033] When the second ceramic composition is incorporated into the dielectric composition of the present invention, preferably, the first ceramic composition accounts for about 50-95 wt.%, the glass composition accounts for about 5-20 wt.%, CuO accounts for about 3 wt.% or less, and the second ceramic composition accounts for about 30 wt.% or less. When the content of the second ceramic composition is in excess of about 30 wt.%, the sinterability of the dielectric ceramic composition of the present invention tends to deteriorate. The first ceramic composition is preferably contained in an amount of about 50-95 wt.%. When the content is less than about 50 wt.% (or when the glass composition is incorporated in an amount of more than about 20 wt.%), the sintered property of the ceramic composition (or the dielectric constant) tends to deteriorate; whereas when the content of the first ceramic composition is in excess of about 95 wt.%, the sintered property of the ceramic composition may also deteriorate.

[0034] As one embodiment of the ceramic electronic parts of the present invention, an LC filter will next be described with reference to Figs. 2 through 4.

[0035] A paste composition is prepared by adding an organic vehicle to the powder composition corresponding to the dielectric ceramic composition of the present invention, and the paste composition is formed into a ceramic green sheet having a thickness of, e.g., 40  $\mu\text{m}$  through a casting method by use of a doctor blade. The sheet is dried and punched to provide a piece having a predetermined size.

[0036] As shown in Fig. 2, via-holes 14 are formed by use of, e.g., a silver paste in the obtained ceramic green sheets 13, if required, and capacitor patterns 15 and coil patterns 16 are subsequently formed by use of, e.g., a silver paste through screen printing. Then, the green sheets are laminated and pressed, to form a laminated sheet.

[0037] The laminated sheet is fired at, e.g., 900°C, then outer contacts 17, 18, 19, and 20 are formed, to thereby obtain an LC filter 10 having a capacitor C1 and coils L1 and L2 therein. Fig. 4 shows an equivalent circuit of the LC filter 10.

[0038] Since the LC filter 10 employs the dielectric ceramic composition of the present invention as a dielectric ceramic layer, it can be produced by simultaneous sintering with an electrically conductive material as an internal conductor layer containing, as a primary component, one of a low-specific-resistance metal selected from gold, silver, and copper. Moreover, the filter has high-frequency characteristics within a microwave region and a millimeter wave region and excellent temperature stability, and can be sufficiently miniaturized.

[0039] In addition to an LC filter shown in Figs. 2 through 4, examples of the ceramic electronic parts of the present invention include chip parts such as LC resonators, laminated chip capacitors, and chip antennas; and ceramic substrates (or ceramic multilayered substrates) such as ceramic substrates for hybrid ICs, VOCs, multichip modules, ceramic packages, etc.

[0040] In addition to a method for producing the ceramic electronic parts of the present invention by shaping the dielectric ceramic composition of the present invention into a green sheet, laminating, and firing; the ceramic electronic parts may be produced by forming a paste composition of the dielectric ceramic composition of the present invention and printing the paste composition to a thick film.

## EXAMPLES

[0041] The dielectric ceramic composition of the present invention will next be described by way of examples.

## Production of First Ceramic Compositions

[0042] BaCO<sub>3</sub>, TiO<sub>2</sub>, Nd<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, Pr<sub>2</sub>O<sub>3</sub>, and Sm<sub>2</sub>O<sub>3</sub> were weighed and mixed together, to obtain mixtures having compositional ratios with regard to BaO, TiO<sub>2</sub>, and REO<sub>3/2</sub> indicated in the columns showing primary components in Table 1. Then, PbO powder was added to each of the above mixtures so as to realize a compositional ratio (parts by weight based on 100 parts of a primary component) indicated in the column showing a secondary component in Table 1, and the resultant mixture was mixed thoroughly. The mixture was calcined at 1150°C for one hour to form a calcined compact, which was then crushed and mixed. The mixture was then fired at 1300-1400°C, to thereby obtain a ceramic. Ceramic compositions S1 through S25 shown in Table 1 were produced by crushing the corresponding ceramics again. The obtained ceramics were subjected to measurement of relative dielectric constant, Q value, and temperature coefficient of change in capacitance. Results of the measurement are shown in Table 1. These first ceramic compositions were used to prepare dielectric ceramic compositions shown below.

Table 1

First ceramic composition No.	Primary component (mole%)			Secondary component (parts by weight)	Relative dielectric constant (ε)	Q value at 1 GHz	Temperature coefficient of dielectric constant (ppm/°C)
	BaO	TiO <sub>2</sub>	ReO <sub>3/2</sub>				
S1	10	63	Nd:27	13	95	5000	-5
S2	15	70	Nd:15	13	85	2500	-80
S3	15	55	Nd:30	13	80	3000	-100
S4	5	70	Nd:25	13	65	4000	-70
S5	5	55	Nd:40	13	54	2200	+20
S6	20	60	Nd:20	13	105	3500	-100
S7	10	75	Nd:15	13	72	3000	-120
S8	2	65	Nd:33	13	50	2500	+10
S9	10	50	Nd:40	13	47	2400	+50
S10	10	63	Nd:27	0	65	3500	+30
S11	10	63	Nd:27	3	80	4000	+30
S12	10	63	Nd:27	20	100	5000	-30
S13	10	63	Nd:27	25	90	900	-100
S14	13	65	Nd:22	0	69	3400	-20
S15	13	60	Nd:27	0	60	3600	+20
S16	20	60	Nd:20	0	75	2000	-100
S17	2	65	Nd:33	0	35	2500	+40
S18	10	63	La:27	13	100	4000	-20
S19	10	63	Pr:27	13	97	4500	-15
S20	10	63	Sm:27	13	92	5000	0
S21	10	63	27 (La/ Nd=0.5/0.5)	13	97	5000	-10
S22	10	63	27 (Pr/ Nd=0.25/0.75)	13	96	5000	-10
S23	13	65	22 (Pr/ Nd=0.25/0.75)	13	101	4000	-10

Table 1 (continuation)

First ceramic composition No.	Primary component (mole%)			Secondary component (parts by weight)	Relative dielectric constant ( $\epsilon$ )	Q value at 1 GHz	Temperature coefficient of dielectric constant (ppm/°C)
	BaO	TiO <sub>2</sub>	ReO <sub>3/2</sub>				
S24	13	65	22 (Pr/Nd=0.5/0.5)	13	100	4500	-5
S25	10	63	27 (Sm/Nd=0.5/0.5)	13	94	5000	-5
S26	10	45	Nd:45	13	43	2000	+60
S27	10	63	27 (Pr/Nd=0.5/0.5)	13	100	4500	-5

Production of Glass Compositions

**[0043]** B<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, BaO, SrO, CaO, MgO, and Li<sub>2</sub>O were weighed and thoroughly mixed together, to obtain mixtures having compositional ratios indicated in Table 2. Each of the mixtures was melted at 1100-1400°C and quenched by pouring into water, then wet-milled to thereby obtain glass compositions G1 through G31.

Table 2

Glass composition No.	Alkaline earth metal oxide RO					B <sub>2</sub> O <sub>3</sub> (wt%)	SiO <sub>2</sub> (wt%)	Li <sub>2</sub> O (wt%)
	Total amount of RO	Proportions of respective components in RO (wt%)						
		BaO	SrO	CaO	MgO			
G1	61	82	11	5	2	14	23	2
G2	30	82	11	5	2	29	39	2
G3	40	82	11	5	2	25	33	2
G4	80	82	11	5	2	5	13	2
G5	90	82	11	5	2	3	5	2
G6	67	82	11	5	2	1	30	2
G7	66	82	11	5	2	3	29	2
G8	50	82	11	5	2	30	18	2
G9	44	82	11	5	2	40	14	2
G10	70	82	11	5	2	20	8	2
G11	68	82	11	5	2	17	13	2
G12	40	82	11	5	2	8	50	2
G13	30	82	11	5	2	8	60	2
G14	63	82	11	5	2	14	23	0
G15	62.5	82	11	5	2	14	23	0.5
G16	62	82	11	5	2	14	23	1



# EP 0 926 107 A2

Table 2 (continued)

Glass composition No.	Alkaline earth metal oxide RO					B <sub>2</sub> O <sub>3</sub> (wt%)	SiO <sub>2</sub> (wt%)	Li <sub>2</sub> O (wt%)
	Total amount of RO	Proportions of respective components in RO (wt%)						
		BaO	SrO	CaO	MgO			
G17	57	82	11	5	2	12	21	10
G18	55	82	11	5	2	11	19	15
G19	61	30	35	25	10	14	23	2
G20	61	40	33	24	3	14	23	2
G21	61	95	2	2	1	14	23	2
G22	61	100	0	0	0	14	23	2
G23	61	85	0	13	2	14	23	2
G24	61	45	35	18	2	14	23	2
G25	61	40	45	13	2	14	23	2
G26	61	85	13	0	2	14	23	2
G27	61	50	12	35	2	14	23	2
G28	61	40	13	45	2	14	23	2
G29	61	83	12	5	0	14	23	2
G30	61	60	15	5	20	14	23	2
G31	61	55	15	5	25	14	23	2

## Production of Dielectric Ceramic Compositions

**[0044]** Dielectric ceramic compositions comprising a mixture of a first ceramic composition and a glass composition (and CuO) were prepared, then evaluated.

**[0045]** To each of the thus-obtained first ceramic compositions S1 through S25, a glass composition selected from G1 through G31 was added so as to produce mixtures having compositional ratios indicated in Tables 3 to 5. To each of the mixtures, CuO powder serving as a secondary component was added so as to produce mixtures having compositional proportions indicated in Tables 3 to 5, which were then mixed thoroughly. To the raw mixtures, appropriate amounts of a binder, a plasticizer, and a solvent were added, and the mixtures were kneaded to provide slurries.

**[0046]** Each of the thus-obtained slurries was molded, through a doctor blade coating method, into a sheet having a thickness of 50  $\mu$ m, and the produced ceramic green sheet was cut into pieces having a size of 30 mm X 10 mm. The pieces were laminated and pressed to form a sheet having a thickness of 0.5 mm. Plate-like dielectric ceramics of sample Nos. 1 to 67 listed in Tables 3 to 5 were obtained by firing the corresponding pressed sheets in N<sub>2</sub> at 1000°C for one hour.

**[0047]** The dielectric ceramics obtained as above were subjected to measurement of relative dielectric constant ( $\epsilon$ ), Q value, and temperature coefficient of change in dielectric constant (ppm/°C). The relative dielectric constant was measured at a frequency of 1 MHz. The results of measurement are shown in Tables 3 to 5.

Table 3

Sample No.	First ceramic composition		Glass composition		CuO content (wt%)	Firing temperature (°C)	Relative dielectric constant ( $\epsilon$ )	Q value	Temperature coefficient of dielectric constant (ppm/°C)	Remarks
	No.	Amount (wt%)	No.	Amount (wt%)						
1	S1	90	G1	10	0	1000	60	2500	0	
2	S1	90	G4	10	0	1000	62	2000	-20	
3	S1	88	G4	12	0	1000	63	2000	-30	
*4	S1	88.5	G2	10	1.5	1000	-	-	-	Not sintered
5	S1	88.5	G3	10	1.5	1000	65	4000	-20	
6	S1	88.5	G4	10	1.5	1000	77	3500	-30	
*7	S1	88.5	G5	10	1.5	1000	78	3000	-40	Poor moisture resistance
*8	S1	88.5	G6	10	1.5	1000	-	-	-	Not sintered
9	S1	88.5	G7	10	1.5	1000	70	4500	-10	
10	S1	88.5	G8	10	1.5	1000	75	3000	-15	
*11	S1	88.5	G9	10	1.5	1000	75	3000	-30	Poor moisture resistance
*12	S1	88.5	G10	10	1.5	1000	80	2500	-20	Poor moisture resistance
13	S1	88.5	G11	10	1.5	1000	77	3000	-15	
14	S1	88.5	G12	10	1.5	1000	73	3500	-5	
*15	S1	88.5	G13	10	1.5	1000	-	-	-	Not sintered

\*\*\*: outside the scope of the invention

Table 3 (continued)

Sample No.	First ceramic composition		Glass composition		CuO content (wt%)	Firing temperature (°C)	Relative dielectric constant ( $\epsilon$ )	Q value	Temperature coefficient of dielectric constant (ppm/°C)	Remarks
	No.	Amount (wt%)	No.	Amount (wt%)						
*16	S1	88.5	G14	10	1.5	1000	-	-	-	Not sintered
17	S1	88.5	G15	10	1.5	1000	70	2500	+10	
18	S1	88.5	G16	10	1.5	1000	72	4500	0	
19	S1	88.5	G17	10	1.5	1000	77	3000	-30	
*20	S1	88.5	G18	10	1.5	1000	78	2500	-30	Poor moisture resistance
21	S14	88.5	G1	10	1.5	1000	53	3000	-25	
22	S15	88.5	G1	10	1.5	1000	48	3100	+15	
23	S16	88.5	G1	10	1.5	1000	60	1700	-120	
24	S17	88.5	G1	10	1.5	1000	27	1500	+35	

\*\*\*: outside the scope of the invention

Table 4

Sample No.	First ceramic composition		Glass composition		CuO content (wt%)	Firing temperature (°C)	Relative dielectric constant ( $\epsilon$ )	Q value	Temperature coefficient of dielectric constant (ppm/°C)	Remarks
	No.	Amount (wt%)	No.	Amount (wt%)						
25	S1	88.5	G1	10	1.5	1000	75	4000	-10	
26	S2	88.5	G1	10	1.5	1000	65	2000	-50	
27	S3	88.5	G1	10	1.5	1000	60	2300	-70	
28	S4	88.5	G1	10	1.5	1000	55	3000	-70	
29	S5	88.5	G1	10	1.5	1000	50	2000	0	
30	S6	88.5	G1	10	1.5	1000	80	2500	-120	
31	S7	88.5	G1	10	1.5	1000	55	2000	-150	
32	S8	88.5	G1	10	1.5	1000	35	1500	-10	
33	S9	88.5	G1	10	1.5	1000	30	1500	+20	
34	S10	88.5	G1	10	1.5	1000	50	3000	0	
35	S11	88.5	G1	10	1.5	1000	65	4000	+10	
36	S12	88.5	G1	10	1.5	1000	80	2000	-20	
37	S13	88.5	G1	10	1.5	1000	70	1000	-150	
38	S1	88.5	G19	10	1.5	1000	-	-	-	Insufficiently sintered
39	S1	88.5	G20	10	1.5	1000	67	4000	+10	
40	S1	88.5	G21	10	1.5	1000	77	4000	-20	
41	S1	88.5	G22	10	1.5	1000	78	3700	-25	Poor moisture resistance
42	S1	88.5	G23	10	1.5	1000	76	4000	-15	
43	S1	88.5	G24	10	1.5	1000	67	3500	+5	

Table 4 (continued)

Sample No.	First ceramic composition		Glass composition		CuO content (wt%)	Firing temperature (°C)	Relative dielectric constant ( $\epsilon$ )	Q value	Temperature coefficient of dielectric constant (ppm/°C)	Remarks
	No.	Amount (wt%)	No.	Amount (wt%)						
44	S1	88.5	G25	10	1.5	1000	-	-	-	Insufficiently sintered
45	S1	88.5	G26	10	1.5	1000	75	4200	-10	
46	S1	88.5	G27	10	1.5	1000	65	4000	+10	
47	S1	88.5	G28	10	1.5	1000	-	-	-	Insufficiently sintered
48	S1	88.5	G29	10	1.5	1000	77	4000	-5	
49	S1	88.5	G30	10	1.5	1000	60	4000	-10	
50	S1	88.5	G31	10	1.5	1000	-	-	-	Insufficiently sintered

Table 5

Sample No.	First ceramic composition		Glass composition		CuO content (wt%)	Firing temperature (°C)	Relative dielectric constant ( $\epsilon$ )	Q value	Temperature coefficient of dielectric constant (ppm/°C)	Remarks
	No.	Amount (wt%)	No.	Amount (wt%)						
51	S1	89.8	G1	10	0.2	1000	70	4000	-5	
52	S1	87	G1	10	3.0	1000	78	3000	-20	
53	S1	87	G1	10	5.0	1000	85	100	+200	
54	S1	95.5	G1	3	1.5	1000	-	-	-	Insufficiently sintered
55	S1	93.5	G1	5	1.5	1000	70	5000	-10	
56	S1	78.5	G1	20	1.5	1000	50	1500	+20	
57	S1	68.5	G1	30	1.5	1000	40	800	+40	Poor moisture resistance
58	S1	87.5	G12	12	0.5	1000	64	4000	-10	
59	S1	87.0	G16	12	1.0	1000	70	3000	-20	
60	S18	88.5	G1	10	1.5	1000	78	3500	-30	
61	S19	88.5	G1	10	1.5	1000	76	4000	-20	
62	S20	88.5	G1	10	1.5	1000	73	4500	-5	
63	S21	88.5	G1	10	1.5	1000	76	4500	-20	
64	S22	88.5	G1	10	1.5	1000	75	4500	-25	
65	S23	88.5	G1	10	1.5	1000	80	3500	-20	
66	S24	88.5	G1	10	1.5	1000	79	4000	-15	
67	S25	88.5	G1	10	1.5	1000	74	4000	-10	

[0048] As is apparent from Tables 3, 4, and 5, dielectric ceramic compositions formed of a mixture comprising a first BaO-TiO<sub>2</sub>-REO<sub>3/2</sub> ceramic composition - wherein RE represents a rare earth element - and a glass composition - which comprises about 13-50 wt.% SiO<sub>2</sub>, about 3-30 wt.% B<sub>2</sub>O<sub>3</sub>, about 40-80 wt.% alkaline earth metal oxide, and about 0.5-10 wt.% Li<sub>2</sub>O - have excellent characteristics; i.e., a high relative dielectric constant, a high Q value, and a low temperature coefficient of change in dielectric constant, as shown for sample Nos. 1 to 3 among sample Nos. 1 to 24. Furthermore, the dielectric compositions are obtained by firing at about 1000°C or less.

[0049] Compositions further containing CuO serving as a secondary component have excellent characteristics; i.e., a high relative dielectric constant, a high Q value, and a low temperature coefficient of change in dielectric constant, as shown for sample Nos. 5, 6, 9, 10, 13, 14, 17 to 19, and 21 to 24 among sample Nos. 1 to 24. Furthermore, more stable dielectric ceramic compositions are obtained by firing at about 1000°C or less. Briefly, incorporation of CuO enhances Q value and relative dielectric constant as shown in comparison between sample No. 1 and sample Nos. 51 to 53, and, although data are not shown, can lower the sintering temperature.

[0050] In contrast, as shown in sample Nos. 4, 7, 8, 11, 12, 15, 16, and 20 among sample Nos. 1 to 24, the dielectric ceramic compositions having a composition falling outside the above-described compositional ranges are not sintered at 1000°C or are sintered insufficiently, to yield poor moisture resistance.

[0051] As shown in sample Nos. 25 to 29, 35, and 36 among sample Nos. 25 to 37, dielectric ceramic compositions having a lower temperature coefficient of change in dielectric constant are obtained by designating the compositional ranges of the first BaO-TiO<sub>2</sub>-REO<sub>3/2</sub> ceramic compositions as xBaO-yTiO<sub>2</sub>-zREO<sub>3/2</sub>, wherein x, y, and z are each based on mole% and are represented by  $5 \leq x \leq 15$ ,  $52.5 \leq y \leq 70$ , and  $15 \leq z \leq 42.5$ ; and  $x + y + z = 100$ , and incorporating about 20 parts by weight or less of PbO to 100 parts by weight of the corresponding first ceramic compositions.

[0052] Preferably, the alkaline earth metal oxide contained in the glass compositions comprises BaO and at least one species selected from the group consisting of SrO, CaO, and MgO, and the compositional ratio thereof lies within the following ranges: about 35 wt.% or less for SrO; about 35 wt.% or less for CaO; about 20 wt.% or less for MgO; and about 40-95 wt.% for BaO, as shown in sample Nos. 39, 40, 42, 43, 45, 46, 48, and 49 among sample Nos. 38 to 50.

[0053] Preferably, the proportions of the first ceramic composition, glass composition, and CuO are respectively about 80-95 wt.%, about 5-20 wt.%, and about 3 wt.% or less, as shown in sample Nos. 51, 52, 55, 58, and 59 among sample Nos. 51 to 59. CuO serving as a secondary component may be incorporated by adding CuO powder into a mixture of the first ceramic composition and the glass composition as shown in the above examples, as well as by mixing a glass composition containing CuO prepared in advance and the ceramic composition. In either case, the same effect can be obtained.

[0054] Moreover, as shown in sample Nos. 60 to 67, dielectric ceramic compositions having excellent characteristics; i.e., a high relative dielectric constant, a high Q value, and a low temperature coefficient of change in dielectric constant, are produced by firing at about 1000°C or less, when La, Pr, or Sm rather than Nd is used as RE, i.e., a rare earth element, of a BaO-TiO<sub>2</sub>-REO<sub>3/2</sub> ceramic composition. Therefore, examples of rare earth elements RE, which may be used singly or in combination, include Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu.

[0055] Dielectric ceramic compositions comprising a mixture of a first ceramic composition, a glass composition, and a second dielectric ceramic composition (and CuO) were prepared, then evaluated.

[0056] An appropriate amount of CuO powder was added to the first ceramic compositions shown in Table 1 and the glass compositions shown in Table 2.

[0057] To each of the thus-obtained mixtures, TiO<sub>2</sub>, CaTiO<sub>3</sub>, SrTiO<sub>3</sub>, and Nd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> serving as second ceramic compositions were then added so as to produce mixtures having compositional proportions indicated in Tables 6 to 11, which were then mixed thoroughly. To the raw mixtures, an appropriate amount of an organic vehicle such as a binder, a plasticizer, and a solvent were added, and the mixtures were kneaded to provide slurries.

[0058] Each of the thus-obtained slurries was molded, through a doctor blade coating method, into a sheet having a thickness of 50 μm, and the produced ceramic green sheet was cut into pieces having a size of 30 mm X 10 mm. The pieces were laminated and pressed to form a sheet having a thickness of 0.5 mm. Dielectric ceramics of samples Nos. 68 to 132 listed in Tables 6 to 11 were obtained by firing the corresponding pressed sheets in air at 1000°C or less for one hour.

[0059] The dielectric ceramics obtained as above were subjected to measurement of relative dielectric constant (ε), Q value, and temperature coefficient of change in dielectric constant (ppm/°C). The relative dielectric constant was measured at a frequency of 1 MHz. The results of measurement are shown in Tables 6 to 11.

Tabl 6A

Sample No.	First ceramic composition		Glass composition		Second ceramic composition		CuO (wt%)
	No.	Amount (wt%)	No.	Amount (wt%)	Species	Amount (wt%)	
68	S1	95.5	G1	3.5	TiO <sub>2</sub>	0.5	0.5
69	S1	94.0	G1	5	TiO <sub>2</sub>	0.5	0.5
70	S1	68.5	G1	20	TiO <sub>2</sub>	10	1.5
71	S1	58.5	G1	30	TiO <sub>2</sub>	10	1.5
72	S1	80	G1	10	TiO <sub>2</sub>	10	0
73	S1	77.0	G1	10	TiO <sub>2</sub>	10	3.0
74	S1	75.0	G1	10	TiO <sub>2</sub>	10	5.0
75	S1	86.5	G1	10	TiO <sub>2</sub>	2	1.5
76	S1	78.5	G1	10	TiO <sub>2</sub>	10	1.5
77	S1	58.5	G1	10	TiO <sub>2</sub>	30	1.5
78	S1	48.5	G1	10	TiO <sub>2</sub>	40	1.5
79	S1	86.5	G1	10	CaTiO <sub>3</sub>	2	1.5
80	S1	58.5	G1	10	CaTiO <sub>3</sub>	30	1.5
81	S1	48.5	G1	10	CaTiO <sub>3</sub>	40	1.5
82	S1	86.5	G1	10	SrTiO <sub>3</sub>	2	1.5
83	S1	58.5	G1	10	SrTiO <sub>3</sub>	30	1.5
84	S1	48.5	G1	10	SrTiO <sub>3</sub>	40	1.5
85	S1	78.5	G1	10	SrTiO <sub>3</sub> /TiO <sub>2</sub>	5/5	1.5
86	S1	48.5	G1	10	SrTiO <sub>3</sub> /TiO <sub>2</sub>	20/20	1.5
87	S1	83.5	G1	10	Nd <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>	5	1.5

Table 6B

Sample No.	First ceramic composition		Glass composition		Second ceramic composition		CuO (wt%)
	No.	Amount (wt%)	No.	Amount (wt%)	Species	Amount (wt%)	
88	S1	78.5	G1	10	Nd <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>	10	1.5
89	S1	58.5	G1	10	Nd <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>	30	1.5
90	S1	48.5	G1	10	Nd <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>	40	1.5
91	S1	58.5	G1	10	TiO <sub>2</sub>	30	1.5
92	S1	48.5	G1	10	TiO <sub>2</sub>	40	1.5
93	S1	86.5	G1	10	CaTiO <sub>3</sub>	2	1.5
94	S1	58.5	G1	10	CaTiO <sub>3</sub>	30	1.5
95	S1	48.5	G1	10	CaTiO <sub>3</sub>	40	1.5
96	S1	86.5	G1	10	SrTiO <sub>3</sub>	2	1.5
97	S1	58.5	G1	10	SrTiO <sub>3</sub>	30	1.5
98	S1	48.5	G1	10	SrTiO <sub>3</sub>	40	1.5



EP 0 926 107 A2

Table 6B (continued)

Sample No.	First ceramic composition		Glass composition		Second ceramic composition		CuO (wt%)
	No.	Amount (wt%)	No.	Amount (wt%)	Species	Amount (wt%)	
99	S1	78.5	G1	10	SrTiO <sub>3</sub> /TiO <sub>2</sub>	5/5	1.5
100	S1	48.5	G1	10	SrTiO <sub>3</sub> /TiO <sub>2</sub>	20/20	1.5
101	S1	83.5	G1	10	Nd <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>	5	1.5
102	S1	78.5	G1	10	Nd <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>	10	1.5
103	S1	58.5	G1	10	Nd <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>	30	1.5
104	S1	48.5	G1	10	Nd <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>	40	1.5

Table 7A

Sample No.	Firing temperature (°C)	Relative dielectric constant (ε)	Q value	Temperature coefficient of dielectric constant (ppm/°C)	Remarks
68	1000	-	-	-	Insufficiently sintered
69	1000	83	5000	-60	
70	1000	53	1600	-80	
71	1000	45	1000	-60	Low ε
72	1000	75	2800	-50	
73	1000	80	3500	-60	
74	1000	110	200	+150	Low Q value
75	1000	76	4000	-20	
76	1000	78	4100	-50	
77	1000	86	2700	-120	
78	1000	-	-	-	Insufficiently sintered
79	1000	78	3800	-30	
80	1000	90	2500	-180	
81	1000	-	-	-	Insufficiently sintered
82	1000	79	3500	-40	
83	1000	120	2000	-250	
84	1000	-	-	-	Insufficiently sintered
85	1000	95	2500	-100	
86	1000	-	-	-	Insufficiently sintered
87	1000	73	3500	0	

Table 7B

Sample No.	Firing temperatur (°C)	Relative dielectric constant ( $\epsilon$ )	Q valu	T mperatur coeffici nt of dielectric constant (ppm/°C)	Remarks
88	1000	71	3000	+10	
89	1000	62	2000	+30	
90	1000	-	-	-	Insufficiently sintered
91	1000	86	2700	-120	
92	1000	-	-	-	Insufficiently sintered
93	1000	78	3800	-30	
94	1000	90	2500	-180	
95	1000	-	-	-	Insufficiently sintered
96	1000	79	3500	-40	
97	1000	120	2000	-250	
98	1000	-	-	-	Insufficiently sintered
99	1000	95	2500	-100	
100	1000	-	-	-	Insufficiently sintered
101	1000	73	3500	0	
102	1000	71	3000	+10	
103	1000	62	2000	+30	
104	1000	-	-	-	Insufficiently sintered

Table 8

Sample No.	First ceramic composition		Glass composition		Second ceramic composition		CuO (wt%)
	No.	Amount (wt%)	No.	Amount (wt%)	Species	Amount (wt%)	
105	S2	78.5	G1	10	TiO <sub>2</sub>	10	1.5
106	S3	78.5	G1	10	TiO <sub>2</sub>	10	1.5
107	S4	78.5	G1	10	TiO <sub>2</sub>	10	1.5
108	S5	78.5	G1	10	TiO <sub>2</sub>	10	1.5
109	S6	78.5	G1	10	TiO <sub>2</sub>	10	1.5
110	S7	78.5	G1	10	TiO <sub>2</sub>	10	1.5
111	S8	78.5	G1	10	TiO <sub>2</sub>	10	1.5
112	S26	78.5	G1	10	TiO <sub>2</sub>	10	1.5
113	S10	78.5	G1	10	TiO <sub>2</sub>	10	1.5
114	S11	78.5	G1	10	TiO <sub>2</sub>	10	1.5

# EP 0 926 107 A2

Table 8 (continued)

Sample No.	First ceramic composition		Glass composition		Second ceramic composition		CuO (wt%)
	No.	Amount (wt%)	No.	Amount (wt%)	Species	Amount (wt%)	
115	S12	78.5	G1	10	TiO <sub>2</sub>	10	1.5
116	S13	78.5	G1	10	TiO <sub>2</sub>	10	1.5
117	S19	78.5	G1	10	TiO <sub>2</sub>	10	1.5
118	S20	78.5	G1	10	TiO <sub>2</sub>	10	1.5
119	S27	78.5	G1	10	TiO <sub>2</sub>	10	1.5

Table 9

Sample No.	Firing temperature (°C)	Relative dielectric constant ( $\epsilon_r$ )	Q value	Temperature coefficient of dielectric constant (ppm/°C)	Remarks
105	1000	68	1500	-120	
106	1000	64	2000	-150	
107	1000	53	2800	-120	
108	1000	45	1200	-30	
109	1000	90	2500	-160	
110	1000	58	2000	-180	
111	1000	37	900	-40	Low Q value
112	1000	30	900	0	Low Q value
113	1000	50	2500	-10	
114	1000	65	2800	0	
115	1000	85	3000	-75	
116	1000	75	500	-150	Low Q value
117	1000	80	3500	-60	
118	1000	75	3800	-40	
119	1000	82	3500	-45	

Table 10

Sample No.	First ceramic composition		Glass composition		Second ceramic composition		CuO (wt%)
	No.	Amount (wt%)	No.	Amount (wt%)	Species	Amount (wt%)	
120	S1	78.5	G2	10	TiO <sub>2</sub>	10	1.5
121	S1	78.5	G3	10	TiO <sub>2</sub>	10	1.5
122	S1	78.5	G4	10	TiO <sub>2</sub>	10	1.5
123	S1	78.5	G5	10	TiO <sub>2</sub>	10	1.5
124	S1	78.5	G6	10	TiO <sub>2</sub>	10	1.5
125	S1	78.5	G8	10	TiO <sub>2</sub>	10	1.5
126	S1	78.5	G9	10	TiO <sub>2</sub>	10	1.5
127	S1	78.5	G12	10	TiO <sub>2</sub>	10	1.5

Table 10 (continued)

Sample No.	First ceramic composition		Glass composition		Second ceramic composition		CuO (wt%)
	No.	Amount (wt%)	No.	Amount (wt%)	Species	Amount (wt%)	
128	S1	78.5	G13	10	TiO <sub>2</sub>	10	1.5
129	S1	78.5	G14	10	TiO <sub>2</sub>	10	1.5
130	S1	78.5	G15	10	TiO <sub>2</sub>	10	1.5
131	S1	78.5	G17	10	TiO <sub>2</sub>	10	1.5
132	S1	78.5	G18	10	TiO <sub>2</sub>	10	1.5

Table 11

Sample No.	Firing temperature (°C)	Relative dielectric constant ( $\epsilon$ )	Q value	Temperature coefficient of dielectric constant (ppm/°C)	Remarks
120	1000	-	-	-	Not sintered
121	1000	75	3500	-50	
122	1000	80	3700	-53	
123	1000	81	3800	-54	Moisture resistance: Not good
124	1000	-	-	-	Not sintered
125	1000	80	3700	-50	
126	1000	81	3800	-52	Moisture resistance: Not good
127	1000	73	3300	-45	
128	1000	-	-	-	Not sintered
129	1000	-	-	-	Not sintered
130	1000	70	2500	-40	
131	1000	81	2000	-50	
132	1000	82	1700	-54	Moisture resistance: Not good

[0060] As is apparent from Tables 6 to 11, the temperature characteristics of the dielectric ceramic compositions can be preset to desired values more effectively by incorporating at least one species of a second ceramic composition selected from the group consisting of TiO<sub>2</sub>, CaTiO<sub>3</sub>, SrTiO<sub>3</sub>, and Nd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> into a dielectric ceramic composition comprising a mixture of a first BaO-TiO<sub>2</sub>-REO<sub>3/2</sub> ceramic composition (wherein RE represents a rare earth element) and a glass composition, wherein the glass composition comprises about 13-50 wt.% SiO<sub>2</sub>, about 3-30 wt.% B<sub>2</sub>O<sub>3</sub>, about 40-80 wt.% alkaline earth metal oxide, and about 0.5-10 wt.% Li<sub>2</sub>O. Briefly, target temperature characteristics of the dielectric compositions can be realized through incorporation of TiO<sub>2</sub>, CaTiO<sub>3</sub>, and SrTiO<sub>3</sub> having a negative temperature coefficient of dielectric constant or Nd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> having a positive temperature coefficient thereof as secondary components.

[0061] In contrast, as in the case of sample No. 120, a dielectric composition containing a lower amount of an alkaline earth metal oxide in the glass composition cannot be sintered at 1000°C; whereas, as in the case of sample No. 123, a dielectric composition containing a higher amount of an alkaline earth metal oxide and a lower amount of SiO<sub>2</sub> has unsatisfactory moisture resistance. As in the case of sample No. 124, a dielectric composition containing a lower amount of B<sub>2</sub>O<sub>3</sub> in the glass composition cannot be sintered at 1000°C, whereas, as in the case of sample No. 126, a dielectric composition containing a higher amount of B<sub>2</sub>O<sub>3</sub> has unsatisfactory moisture resistance. Moreover, as in the case of sample No. 128, a dielectric composition having a lower content ratio of an alkaline earth metal oxide and

a high content ratio of  $\text{SiO}_2$  in the glass composition cannot be sintered at  $1000^\circ\text{C}$ ; whereas, as in the case of sample No. 129, a dielectric composition not containing a predetermined amount of  $\text{Li}_2\text{O}$  in the glass composition cannot be sintered and a dielectric ceramic composition containing an excessive amount of  $\text{Li}_2\text{O}$  has unsatisfactory moisture resistance as in the case of sample No. 132.

**[0062]** As in the case of sample No. 68, the sintered property of a dielectric ceramic composition having a higher content ratio of the first ceramic composition and having a lower content ratio of the glass composition tends to deteriorate; whereas as in the case of sample No. 71, the dielectric constant of a dielectric ceramic composition having a higher content ratio of glass composition tends to decrease. As in the case of sample No. 74, the Q value of a dielectric ceramic composition having a higher content ratio of  $\text{CuO}$  in the glass composition tends to decrease.

**[0063]** As in the case of sample Nos. 81, 84, 86, 90, 92, 95, 98, 100, and 104, the sintered property of a dielectric ceramic composition having a lower content ratio of the first ceramic composition and a higher content ratio of the second ceramic composition tends to deteriorate.

**[0064]** Furthermore, as indicated in the case of sample Nos. 109 and 110, a dielectric ceramic composition having a compositional range of the first ceramic composition falling within the domain A or the domain B indicated in Fig. 1 tends to have a greater temperature coefficient. Although examples are not shown here, when the range falls within the domain A, sintering of a ceramic composition tends to be difficult and a porous ceramic might be produced. As in the case of sample Nos. 111 and 112, when a compositional range of the first ceramic composition falls in the domain C and the domain D indicated in Fig. 1, the relative dielectric constant tends to decrease. When the  $\text{PbO}$  content in the first ceramic composition is excessively high, as indicated in sample No. 116, the relative dielectric constant tends to decrease.

**[0065]** In the above Tables, the term "not sintered" denotes that firing at a predetermined temperature can never be performed, and the term "insufficiently sintered" denotes that firing is completed insufficiently under the above conditions and may be possible by modifying the conditions. The term "poor moisture resistance" refers to moisture resistance of a dielectric ceramic composition causing fatal problems and the term "insufficient moisture resistance" refers to moisture resistance that may be insufficient depending on conditions.

**[0066]** As described herein above, the present invention provides a dielectric ceramic composition which is sintered at a temperature lower than the melting point of an electric conductor containing, as a primary component, one of a low-specific-resistance metal selected from gold, silver, and copper. Moreover, there can be obtained a dielectric ceramic composition having a high relative dielectric constant within a high-frequency region, particularly within a microwave region and a millimeter wave region, as well as excellent temperature stability.

**[0067]** Therefore, such a dielectric ceramic composition can be fired simultaneously with a low-specific-resistance internal electrode made of gold, silver, copper, etc., and there can be obtained ceramic electronic parts such as dielectrics and multilayer circuit boards containing such an internal electrode therein and having excellent high-frequency characteristics. Ceramic electronic apparatus such as an LC resonator and an LC filter having a high dielectric constant and a high Q value can be further miniaturized in a lamination method making use of the dielectric ceramic composition.

## Claims

1. A dielectric ceramic composition comprising a mixture of a first  $\text{BaO-TiO}_2\text{-REO}_{3/2}$  system ceramic composition (RE represents a rare earth element) and a glass composition, wherein the glass composition comprises about 13-50 wt.%  $\text{SiO}_2$ , about 3-30 wt.%  $\text{B}_2\text{O}_3$ , about 40-80 wt.% alkaline earth metal oxide, and about 0.5-10 wt.%  $\text{Li}_2\text{O}$ .
2. The dielectric ceramic composition according to Claim 1, which further comprises  $\text{CuO}$  as a secondary component.
3. The dielectric ceramic composition according to Claim 1, wherein the first  $\text{BaO-TiO}_2\text{-REO}_{3/2}$  system ceramic composition is represented by  $x\text{BaO-yTiO}_2\text{-zREO}_{3/2}$  (wherein x, y, and z are based on mole% and satisfy the following relations:  $5 \leq x \leq 15$ ,  $52.5 \leq y \leq 70$ ,  $15 \leq z \leq 42.5$ ; and  $x + y + z = 100$ ), and contains  $\text{PbO}$  in an amount of about 20 parts by weight or less with respect to 100 parts by weight of the first ceramic composition.
4. The dielectric ceramic composition according to Claim 2, wherein the first  $\text{BaO-TiO}_2\text{-REO}_{3/2}$  ceramic composition is represented by  $x\text{BaO-yTiO}_2\text{-zREO}_{3/2}$  (wherein x, y, and z are based on mole% and satisfy the following relations:  $5 \leq x \leq 15$ ,  $52.5 \leq y \leq 70$ ,  $15 \leq z \leq 42.5$ ; and  $x + y + z = 100$ ), and contains  $\text{PbO}$  in an amount of about 20 parts by weight or less with respect to 100 parts by weight of the first ceramic composition.
5. The dielectric ceramic composition according to Claim 1, wherein the alkaline earth metal oxide contained in the glass composition comprises  $\text{BaO}$  and at least one species selected from the group consisting of  $\text{SrO}$ ,  $\text{CaO}$ , and  $\text{MgO}$ , and the compositional proportions of  $\text{SrO}$ ,  $\text{CaO}$ ,  $\text{MgO}$ , and  $\text{BaO}$  fall within the ranges of about 35 wt.% or

less, about 35 wt.% or less, about 20 wt.% or less, and about 40-95 wt.%, respectively.

6. The dielectric ceramic composition according to Claim 2, wherein the alkaline earth metal oxide contained in the glass composition comprises BaO and at least one species selected from the group consisting of SrO, CaO, and MgO, and the compositional proportions of SrO, CaO, MgO, and BaO fall within the ranges of about 35 wt.% or less, about 35 wt.% or less, about 20 wt.% or less, and about 40-95 wt.%, respectively.

7. The dielectric ceramic composition according to any one of Claim 2, wherein the first ceramic composition accounts for about 80-95 wt.%, the glass composition accounts for about 5-20 wt.%, and CuO accounts for about 3 wt.% or less.

8. The dielectric ceramic composition according to Claim 1, which comprises at least one species of a second ceramic composition selected from the group consisting of TiO<sub>2</sub>, CaTiO<sub>3</sub>, SrTiO<sub>3</sub>, and Nd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>.

9. The dielectric ceramic composition according to Claim 2, which comprises at least one species of a second ceramic composition selected from the group consisting of TiO<sub>2</sub>, CaTiO<sub>3</sub>, SrTiO<sub>3</sub>, and Nd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>.

10. The dielectric ceramic composition according to Claim 8, wherein the first ceramic composition accounts for about 50-95 wt.%, the glass composition accounts for 5-20 wt.%, CuO accounts for about 3 wt.% or less, and the second ceramic composition accounts for about 30 wt.% or less.

11. The dielectric ceramic composition according to Claim 9, wherein the first ceramic composition accounts for about 50-95 wt.%, the glass composition accounts for about 5-20 wt.%, CuO accounts for about 3 wt.% or less, and the second ceramic composition accounts for about 30 wt.% or less.

12. A ceramic electronic part which comprises as a dielectric ceramic layer the dielectric ceramic composition as recited in Claim 1.

13. A ceramic electronic part which comprises as a dielectric ceramic layer the dielectric ceramic composition as recited in Claim 2.

14. A ceramic electronic part comprising:

a ceramic layer;

an internal electrode including at least one of Au, Ag and Cu, said electrode is disposed in said ceramic layer; wherein said ceramic layer and said internal electrode formed by firing a ceramic green sheet and metal paste associated with said green sheet at a temperature about 1000°C or less.

15. A method of producing a ceramic composition comprising the steps of:

firing raw materials of BaO-TiO<sub>2</sub>-REO<sub>3/2</sub> system ceramic composition;

heating raw materials of a glass composition including SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, alkaline earth metal oxide, and Li<sub>2</sub>O;

abruptly cooling said heated materials;

mixing powder of said ceramic composition and said glass composition with organic binder;

forming ceramic green sheet of said mixture;

firing said green sheet;

wherein said glass composition comprises about 13-50 wt.% SiO<sub>2</sub>, about 3-30 wt.% B<sub>2</sub>O<sub>3</sub>, about 40-80 wt.% alkaline earth metal oxide, and about 0.5-10 wt.% Li<sub>2</sub>O in said green sheet.

16. The method of producing a ceramic composition according to claim 15, wherein said step of firing said green sheet is carried out at a temperature of 1000°C or below.

17. The method of producing a ceramic composition according to claim 16, wherein said step of firing said green sheet is carried out for about 1 hour.

18. The method of producing a ceramic composition according to claim 16, wherein said step of firing said green sheet is carried out in nitrogen gas.

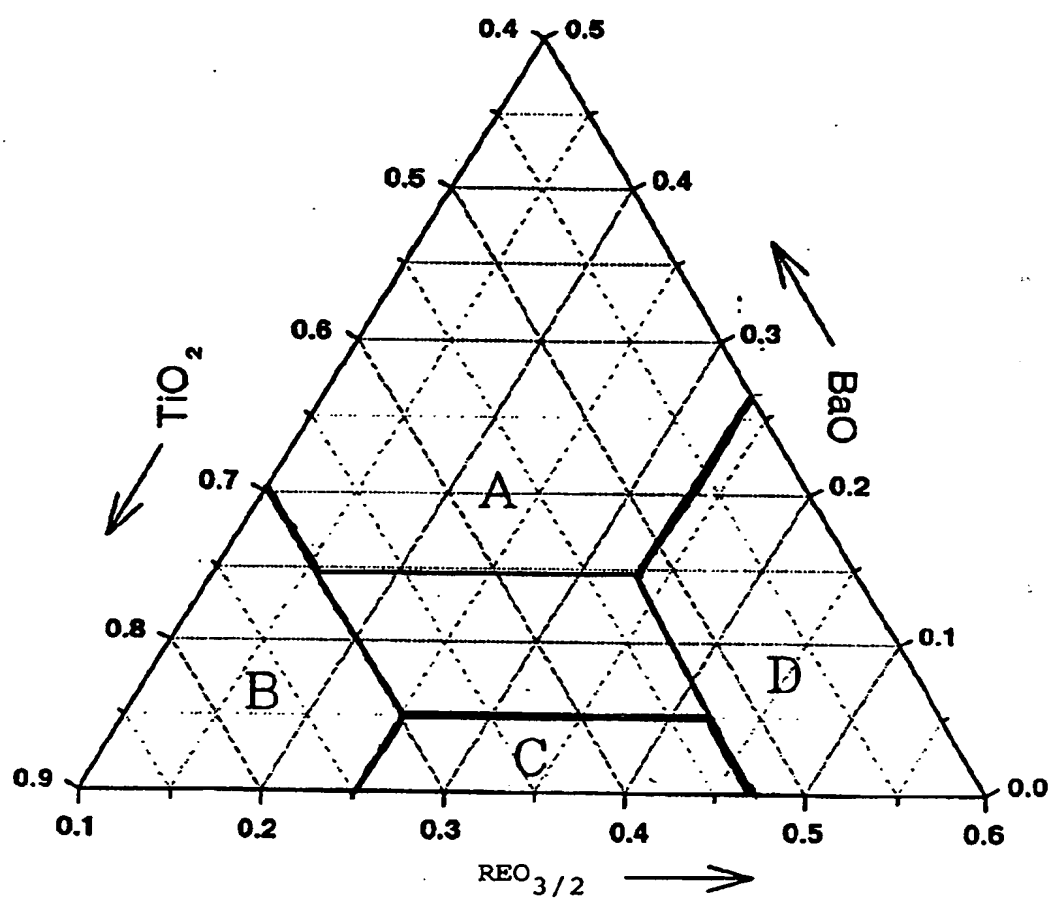
Fig. 1

Fig. 2

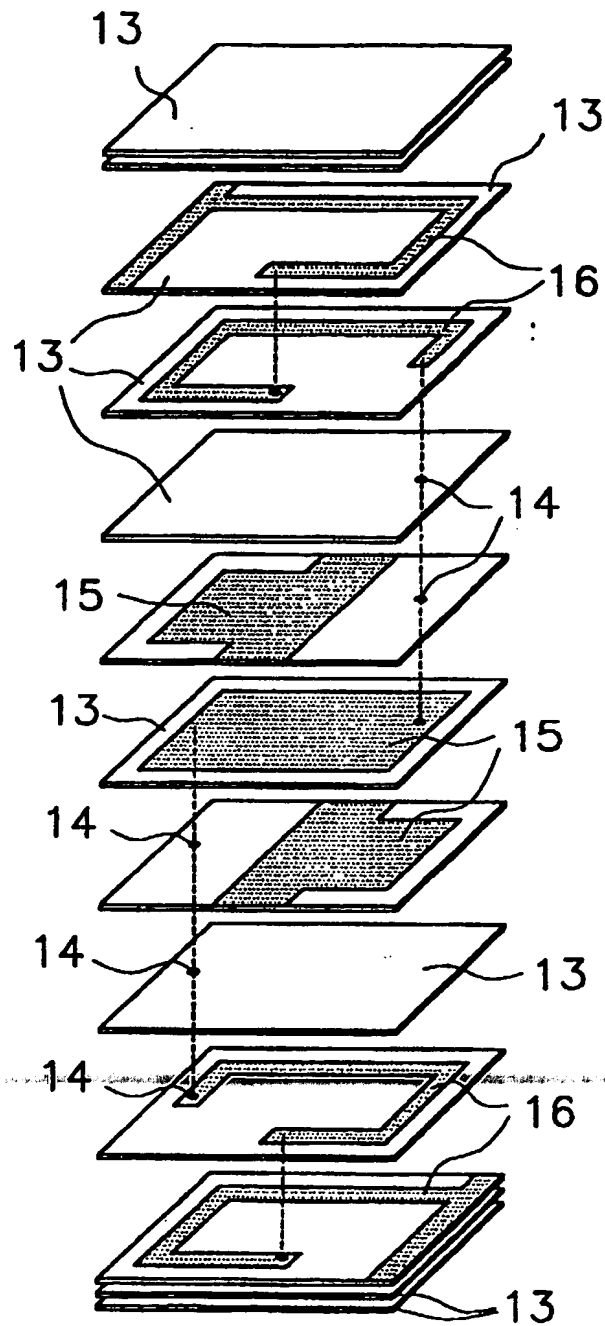




Fig. 3

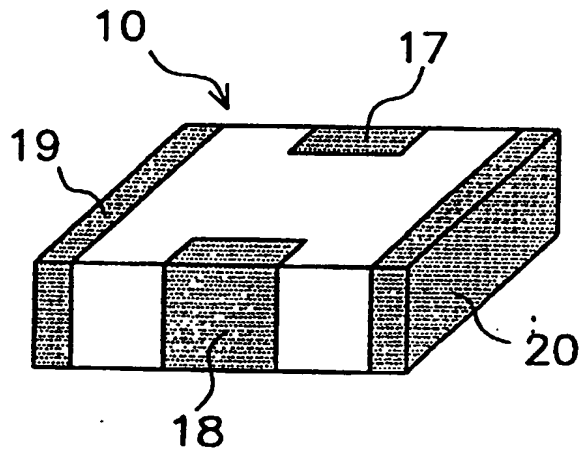
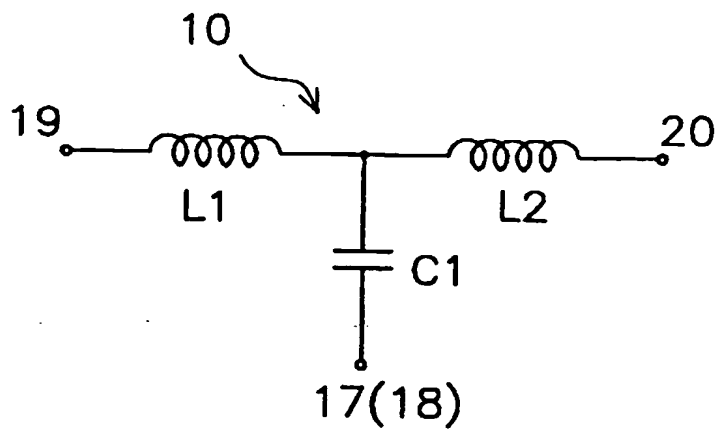


Fig. 4



**THIS PAGE BLANK (USPTO)**